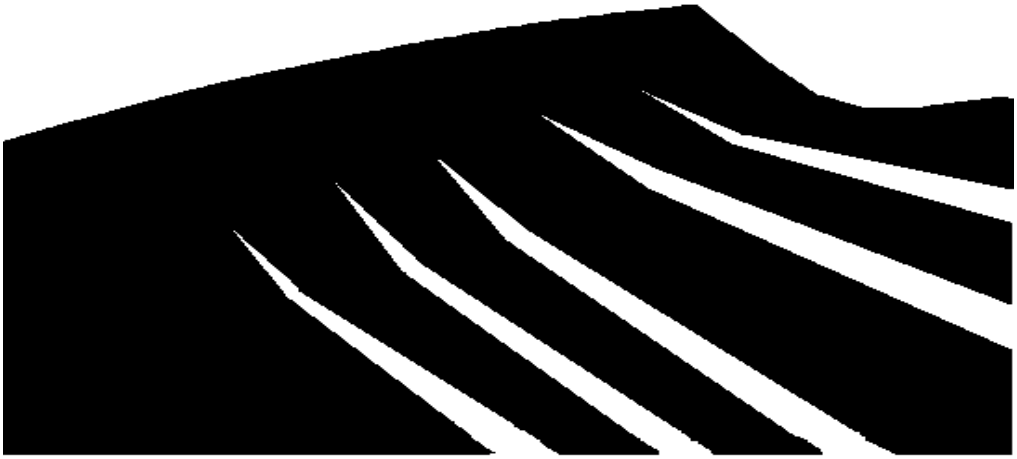
SORPTION AND DESORPTION DETERMINATIONS BY A BATCH SAMPLE TECHNIQUE WITHIN THE CONTROLLED ATMOSPHERE OF A GLOVEBOX FOR THE DYNAMIC TRANSPORT TASK

LOS ALAMOS

QUALITY PROGRAM



APPROVAL FOR RELEASE

I. TRIAY - PREPARER Signature on file	DATE
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M. J. CLEVENGER - QUALITY ASSURANCE PROJECT LEADER Signature on file	DATE

Los Alamos
Yucca Mountain Site Characterization Project

HISTORY OF REVISION

REVISION NO.	EFFECTIVE DATE	PAGES REVISED	REASON FOR CHANGE
R0	08/08/94	N/A	Not procedure.
R1	12/10/96	All	Revised to comply with LANL-YMP-QP-06.3 requirements.

SORPTION AND DESORTION DETERMINATIONS BY A BATCH SAMPLE TECHNIQUE WITHIN THE CONTROLLED ATMOSPHERE OF A GLOVEBOX FOR THE DYNAMIC TRANSPORT TASK

1.0 PURPOSE

The detailed technical procedure (DP) describes the use of a glovebox to determine sorption coefficients for the distribution of various species between geologic materials and natural or synthetic waters within a controlled environment.

2.0 SCOPE

This procedure applies to sorption and desorption studies for the Yucca Mountain Project (YMP) at Los Alamos National Laboratory (Los Alamos).

3.0 REFERENCES

LANL-YMP-QP-02.7, Personnel Training
LANL-YMP-QP-03.5, Documenting Scientific Investigations
LANL-YMP-QP-08.1, Identification and Control of Samples
LANL-YMP-QP-12.3, Control of Measuring and Test Equipment and Standards
LANL-YMP-QP-17.6, Records Management
LANL-CST-DP-63, Preparation of NTS Core Samples for Crushed Rock Experiments
LANL-CST-DP-79, Liquid Scintillation Counting of Samples
LANL-CST-DP-86, Sorption and Desorption Determinations by a Batch Sample Technique for the Dynamic Transport Task
LANL-CST-DP-99, Collection of Bulk Well and Spring Water Samples CST Division Environmental Safety and Health Operational Statement

4.0 DEFINITIONS

4.1 Kd Values

The measured sorption or desorption ratio, Kd, is defined as the amount of sorbing or desorbing species per gram of solid divided by the amount of sorbing or desorbing species per ml o solution (at equilibrium).

4.2 Samples

Samples are geologic materials used for laboratory studies as part of the YMP site characterization process. These materials include both pure minerals, tuffs and water.

4.3 Tracer Solution

Tracer solutions are comprised of either synthetic water or natural water from Yucca Mountain along with a specified concentration of the species whose sorption behavior is to be studies (for example, neptunium, plutonium or uranium).

5.0 RESPONSIBILITIES

The following personnel are responsible for the activities identified in Section 6.0 of this procedure.

- Principal Investigator (PI)
- Users of this procedure (D)P

6.0 PROCEDURE

The use of this procedure must be controlled as follows:

- If this procedure cannot be implemented as written, YMP personnel should notify appropriate supervision. If it is determined that a portion of the work cannot be accomplished as described in this QP, or would result in an undesirable situation, that portion of the work will be stopped and not resumed until this procedure is modified, replaced by a new document, or the current work practice is documented in accordance with QP-03.5, Section 6.1.6.
- Employees may use copies of this procedure printed from the controlled document electronic file; however, employees are responsible for assuring that the correct revision of this procedure is used.
- When this procedure becomes obsolete or superseded, it must be destroyed or marked “superseded” to ensure that this document is not used to perform work.

6.1 PRINCIPLE

This procedure can be used to study sorption or desorption in a controlled atmosphere. By varying the concentration of CO_2 in the glovebox atmosphere, solution pH can also be controlled thus allowing experiments to better simulate the natural underground environment at Yucca Mountain or other sites. This procedure can measure a sorption ratio and, if in the sorption equilibrium, the distribution coefficient.

6.2 Equipment and Hardware/Software

The following equipment, or its equivalent, is used in this procedure:

- calibrated analytical balances for inside and outside of the glovebox with a minimum capacity of 100 g and 0.01 sensitivity
- orbital shaker inside glovebox
- 50 ml volume containers with leak-proof caps
- centrifuge capable of 17,000 RCF (Relative Centrifugal Force)
- analytical pipettes
- a glovebox as shown in Attachment 1 (Figures 1, 2, and 3) pH meter within glovebox
- for monitoring glovebox and maintaining atmospheric conditions:
  - $\%CO_2$ and air pressure input gauges
  - internal atmosphere pressure gauges
  - thermometer
  - hygrometer
  - automatic humidity controller
  - humidifier
- liquid scintillation counter

6.2.1 Equipment Malfunctions

Any equipment malfunction during the course of an experiment should be noted and brought to the attention of the PI. The PI will determine if the malfunction invalidates the experimental results.

6.2.2 Safety Considerations

Tracer solutions for these experiments are often radioactive and should be handled in accordance with CST Division Environmental Safety and Health Operational Policy Statement. The CO_2 tanks must be attached to the glovebox by personnel with appropriate Los Alamos safety training. For proper operation of the centrifuges, consult manufacturers' instructions.

6.2.3 Special Handling

There are no special handling requirements.

6.3 Preparatory Verification

6.3.1 Hold Points

There are no hold points for this procedure.

6.3.2 Calibration

Balances used must be calibrated pursuant to QP-12.3. The unique identifier number of each balance used is recorded in the logbook (See Attachment 2).

pH meters are calibrated before and checked after measurements. Required measurements are noted in Attachment 3, sections A48-A60.

All measurements not listed in this attachment as “required” are considered non-critical (e.g., glovebox monitoring instruments).

6.3.3 Environmental Conditions

The glovebox atmosphere is set and maintained as described in 6.5. Steps to minimize cross-contamination of samples are noted in the same section.

6.4 Control of Samples

All samples will be controlled using the following procedures:

- LANL-YMP-QP-08.1, Identification and Control of Samples
- LANL-CST-DP-99, Collection of Bulk Well and Spring Water Samples
- LANL-CST-DP-63, Preparation of NTS Core Samples for Crushed Rock Experiments

6.5 Implementing Procedure

6.5.1 Glovebox set up.

6.5.1.1

The glovebox is set up as shown in Figures #1-3 (Attachment 1). Two gases, room air and CO_2 (with a degree of purity of 95.5%), are introduced from their manifolds through pressure gauges into the rear of the glovebox. CO_2 follows the route on Figure #3 of m-k-i-h-f-e-d, while the air follows the route of g-f-e-d. The valve marked in Figure #3 as e allows the box to be closed off when the desired pH value has been reached. To further close off the box. Figure #3 valves b and r are closed.

6.5.2 Outside the glovebox, weigh an amount of the material (the sample) to be used (for example: a pure mineral, or a tuff from the NTS) into a clean pre-weighed container with a leak-proof cap. Determine and record the weight of the sample and the sample identification (See Attachment 3).

6.5.3 Moving items in and out of the glovebox.

6.5.3.1 When items need to be removed and replaced during the experiment, they pass through the antechamber, but because of inadequate pressure within the glovebox, the chamber is not evacuated. For introducing samples, insure that inner door is sealed before opening outer door. Load tray and then close outer door before opening inner door to limit loss of CO_2 atmosphere within the glovebox. During this exchange, insure that the air / CO_2 mix is flowing to better maintain equilibration levels.

6.5.4 Introduce to the glovebox:

- the samples
- sufficient DI water and acid solution to rinse pH meter electrode between measurements
- enough of the appropriate synthetic or ground water to allow pre-equilibration of the samples in the ratio of 20 ml solution to 1 g sample
- fresh buffers for at least two pH values to calibrate pH meter (buffers shall bracket measured pH values)

6.5.5 Equilibrate synthetic or ground water to be desired pH l evel.

6.5.1.1 Inside the glovebox, the CO_2 / air mixture is bubbled through the equilibration water and the tracer solutions via rubber tubes (Figure #1,f). Fans (Figure#1, a insure equal distribution of CO_2 through-out box and the humidifier and automatic humidity controller (Figure #3, n and o) keep humidity levels high enough to limit evaporation of tracer solutions.

6.5.6 After the water has stabilized at the desired pH level, add a known volume of this water to each of the sample containers from 6.52. Determine the mass of the container after addition of water. Record the mass (See Attachment 4).

6.5.7 Record in the logbook the Julian date the pre-equilibration water was added; the relative rates of CO_2 and air input into the glovebox: the glovebox pressure, humidity, % CO_2, and temperature: and the pH value of the pre-equilibration water (See Attachment 3).

6.5.8 Shake the mixed phases for a period of time determined by the PI (usually 2-14 days). During the shaking phase, turn off the CO_2/air inflow and close the box as described in 6.5.1.

6.5.9 After the pre-equilibration, weigh the sample containers inside the glovebox, recording the Julian date (See Attachment 3).

6.5.10 Remove samples from the glovebox and centrifuge them at 17,000 RCF for 2 hours.

6.5.11 With minimal jarring, return samples to glovebox. Inside glovebox, decant supernatant into other vials. Record mass of vials after decantation, and record the pH value of the supernants (See Attachment 3).

6.5.12 Prepare the tracer solution to be used in this experiment, and document the method used in the CST solution binder.

6.5.13 Introduce tracer solution to glovebox and equilibrate as described in 6.5.4.

6.5.14 After the tracer solution has reached the desired pH level, add a specified volume of tracer to each sample. Record weight, julian date, and glovebox information as per 6.5.6 (See Attachment 3).

6.5.15 Take two aliquots of the tracer (generally 6 ml each), and set them aside in liquid scintillation counting vials. Record the mass of the vials before and after aliquot (See Attachment 4).

6.5.16 Shake the sample containers as per 6.5.7. Note julian date shaking started and ended.

6.5.17 After shaking, weigh the sample containers.

6.5.18 Record the glovebox vital signs again as per 6.5.6.

6.5.19 Before removing samples from glovebox, measure pH values of the two-phase solutions. To minimize cross-contamination, rinse the electrode between measurements, using first an acid solution followed by DI water.

6.5.20 Remove sample contain ers from glovebox and centrifuge at 17,000 RCF for one hour.

6.5.21 Decant supernatant into another set of containers. For desorption experiments, weigh the sample containers after decantation.

6.5.22 Centrifuge the supernatant containers for another hour and then pipette approximately 12 ml into a third set of containers.

6.5.23 Centrifuge the third set of containers for an additional two hours. From these containers, pipette a 6 ml aliquot into labeled scintillation counting vials for analysis.

6.5.24 Add 14 ml Ultima Gold AB liquid scintillation cocktail to each sample and then count according to LANL-CST-DP-79.

6.6 Data Acquisition and Reduction

Calculate the Kd according to the definition given in section 4.0 and as described in LANL-CST-DP-86.

The active recording of data as specified in Attachment 3 will constitute the data acquisition. Computer programs such as word processing editors and spreadsheets will be used for recording and formatting data but are not part of the data acceptance criteria.

6.7 Potential Sources of Error and Uncertainty

When work, as described in this DP, cannot be accomplished or would result in an undesirable situation, the work will be stopped and not resumed until this DP is revised to reflect the correct work practice. However, if the revision of the DP cannot be accomplished in a timely manner, the continuation of the work will be described in accordance with LANL-YMP-QP-03.5.

The responsible PI or his/her designee will determine whether to use the data. If a decision to use the data is made, the justification for this decision must be entered in the investigator's logbook or binder.

7.0 RECORDS

Records generated as a result of this DP are entries in laboratory notebooks or attachments to laboratory notebooks. The documentation should consist of any applicable items identified in Section 6.0 of this procedure. Laboratory notebooks should be kept in accordance with QP-03.5, Documentation of Scientific Results.

All records should be submitted to the Records Processing Center in accordance withQP-17.6, Records Management.

8.0 ACCEPTANCE OF CRITERIA

If non-optional data are recorded as designated in Attachments 2 and 3, and/or if the PI accepts the experimental data, the data will be accepted as qualified for the YMP.

9.0 TRAINING

9.1 All experimenters will be trained under the supervision of qualified personnel.

9.2 Prior to conducting work described in Section 6.0, the user requires training to this procedure.

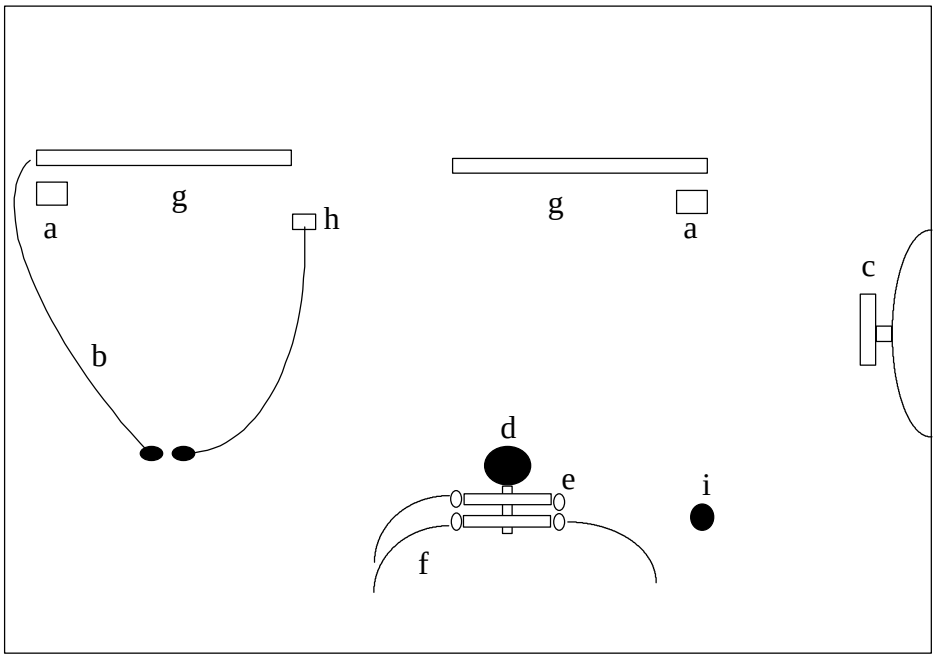
9.3 Training to this procedure is accomplished by “read only”. Training will be documented per OP-02.7.

10.0 ATTACHMENTS

Attachment 1: Figure #1-3 (3 pages)
Attachment 2: Data Sheet (3 pages)
Attachment 3: Spreadsheet (2 pages)

FIGURE #1

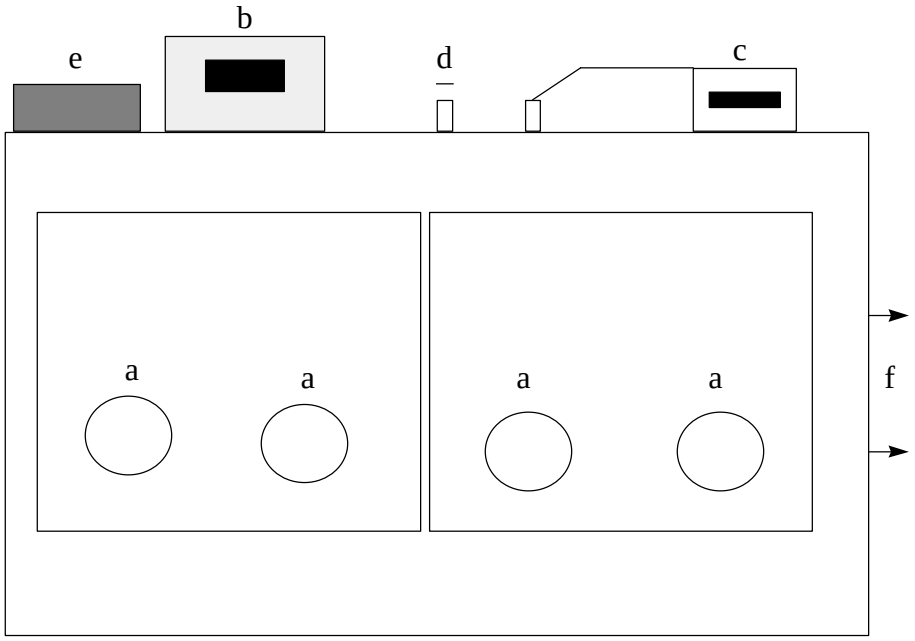
View of back wall inside glove box



a. fans
b. rubber hose leading out to CO_2 % gage
c. door to evacuation chamber
d. inlet for CO_2 / air mixture
e. four valves to control out flow of mixture
f. three rubber tubes for funneling CO_2 / air mix through solutions
g. shelves
h. sensor for automatic humidity control
i. inlet for humidifier hose

FIGURE #2

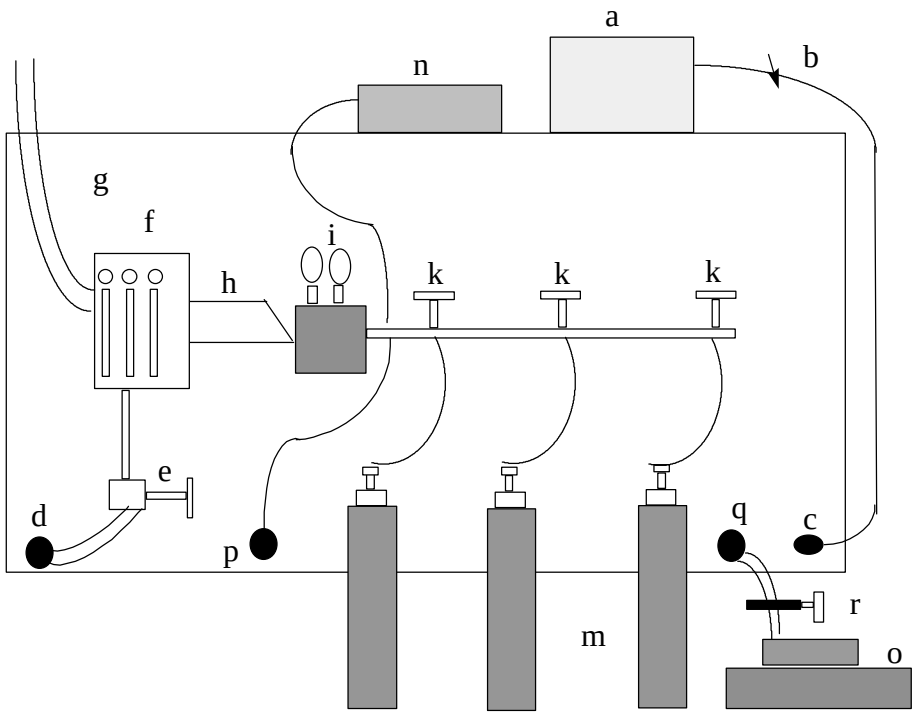
View from front of glove-box



a. glove holes
b. CO_2 gage
c. pressure gage
d. pressure release
e. automatic humidifier control
f. to antechamber and pressure door

FIGURE #3

View from back of glove-box



a. CO_2
b. clamp to close off CO_2 tube from glove-box
c. outlet for CO_2 gage line
d. inlet for CO_2/air mix
e. valve to close off CO_2/air mix
f. liquid pressure gage to determine relative mix of CO_2 and air
g. line in of pressurized air
h. ¼" copper tubing from CO_2 pressure gage
i. CO_2 pressure gage
k. valves to cut off CO_2 flow from each tank
m. CO_2 tanks
n. automatic humidity controller
o. humidifier
p. inlet for a.h.c. probe
q. inlet for humidified air
r. valve to close off tube to humidifier

YUCCA MOUNTAIN DATA INFORMATION SHEET	
Experiment Number	***required***
ID of water used in experiment	***required***
Binder Reference	***required***
Tracer ID	***required***
Binder with Information on Tracer Solution	***required***
Balance Used Before Addition of Radionuclide Tracer	***required***
Balance Used After Addition of Radionuclide Tracer	***required***
Balance Used Within Glovebox	***required***
For Glovebox, Balance Used to Weigh Scintillation Vials and Aliquots	***required***
Mineral Code IDs	***required***
Sieving Information	***required***
Binder with Information on Solid Samples	***required***
Type of Oak Ridge Container Used for Sorption Experiment	***required***
Sorption Procedure Utilized	***required***
Glovebox Information	
Equilibration Water pH Before Adding to OR Tubes	***required***
Glovebox Temperature Before Adding Equilibration Water to OR Tubes, °C	
Glovebox Humidity Before Adding Equilibration Water to OR Tubes, %	
Glovebox Pressure Before Adding Equilibration Water to OR Tubes, Torr	
Glovebox CO_2 Reading Before Adding Equilibration Water to OR Tubes, %	
Arbitrary Glovebox Air Pressure Gage Input Reading Before Adding Equilibration Water to OR Tubes	
Arbitrary Gloxebox CO_2 Pressure Gage Input Reading Before Adding Equilibration Water to OR Tubes	
Glovebox Temperature Before Adding Tracer Solution to OR Tubes, °C	
Glovebox Humidity Before Adding Tracer Solution to OR Tubes, %	
Glovebox Pressure Before Adding Tracer Solution to OR Tubes, Torr	
Glovebox CO_2 Reading Before Adding Tracer Solution to OR Tubes, %	
Arbitrary Glovebox Air Pressure Gage Input Reading Before Adding Tracer Solution to OR Tubes	
Arbitrary Glovebox CO_2 Pressure Gage Input Reading Before Adding Tracer Solution to OR Tubes	

Back-up Equilibration Water pH After Sorption	
Glovebox Temperature After Sorption, °C	
Glovebox Humidity After Sorption, %	
Glovebox Pressure After Sorption, Torr	
Glovebox CO_2 Reading After Sorption, %	
Arbitrary Glovebox Air Pressure Gage Input Reading After Sorption	
Arbitrary Glovebox CO_2 Pressure Gage Input Reading After Sorption	
Glove Box Identification Code	***required***
Hygrometer Used in Glovebox	
Controlled Atmosphere Pressure Gage Used in Glovebox	
CO_2 and Air Input Pressure Gage Used in Glovebox	
Binder Reference for CO_2/Air input Pressure Gage Correlation	YMP SORP/DESORP BINDER III Vol.2 TWS-INC-10-93-06
Pressure for Air Input sccm	
Pressure for CO_2 Input sccm	
pH Measurement	
pH Procedure Used	***required***
pH meter	***required***
ID of pH Meter	***required***
Tracer Solution pH Before Adding to OR Tubes	***required***
Lot Number and Brand for pH 4 Buffer	
Reading for pH 4 Buffer (prior to making measurements)	
Reading for pH 4 Buffer (after making measurements)	
Lot Number and Brand for pH 7 Buffer	***required***
Reading for pH 7 Buffer (prior to making measurements)	***required***
Reading for pH 7 Buffer (after making measurements)	
Lot Number and Brand for pH 10 Buffer	***required***
Reading for pH 10 Buffer (prior to making measurements)	***required***
Reading for pH 10 Buffer (after making measurements)	
Eh Measurement	
Eh Procedure Used	TWS-INC-03-93-01, p. A12-A16
ID of Eh Meter	
Electrodes Used for Eh Measurement	
Zobell Lot Number and Ideal Value	
Zobell Solution preparation date	
Eh of the Zobell Solution (prior to making Measurements), mV	

Eh of the Zobell Solution (after making Measurements), mV	
Temperature Range for Eh Measurements, °C	
Eh of Water Used in the Experiment, mV	
Verification of Liquid Scintillation Counting	
ID of Liquid Scintillation Counter	***required when pertinent***
ID of Standard Counted	***required when pertinent***
Ideal Counts per Minute of Standard Counted	***required when pertinent***
Actual Counts per Minute	***required when pertinent***
ID of Standard Counted	***required when pertinent***
Ideal Counts per Minute of Standard Counted	***required when pertinent***
Actual counts per Minute	***required when pertinent***
Procedure Utilized	***required when pertinent***
Vendor Sample Analysis Information	***required when pertinent***
Vendor Analysis Notebook Reference:	***required when pertinent***
Location of Data	***required***
Experimental Data (notebook #)	***required***
Experimental Data (page(s)	***required***
Reduced Data (optical disk#)	***required***
Reduced Data (subdirectory #)	***required***
Reduced Data (file Name)	***required***

Sample Identification	Experiment No.	Atmosphere	Desired Radionuclide Tracer Solution Concentration CPM/ml or ppm	Description of Solid	Particle Size, micrometers (if sieved)	Sieving Information	Type of Water Used if Wet Sieved
Required	*Required*				*Required*	*Required*	*Required*
Tube + Cap Mass, g	Tube + Cap + Mineral Mass, g	Mineral Mass, g	Tube + Cap + Mineral + Water Mass, g	Water Mass, g	Julian Date Pretreatment Started '94	Julian Date Pretreatment Ended '94	Period of Pretreatment, Days
Required	*Required*		*Required*		*Required*	*Required*	*Required*
Tube + Cap + Mineral + Water (after Pretreatment) Mass, g	% Evaporation during Pretreatment	Tube + Cap + Mineral + Water (after Decantation) Mass, g	pH of Water after Pretreatment	Eh of Water after Pretreatment, mV	Julian Date Tracer Solution was added, '94	Mass after Tracer Solution was added, g	Julian Date Sorption Started "94
Required		*Required*	*Required*		*Required*	*Required*	*Required*
Julian Date Sorption Ended '94	Period of Sorption, Days	Mass after Sorption Ended, g	% Evaporation during Sorption	Tracer Solution pH After sorption (Recorded Inside Glovebox Before Spin-down)	Mass after Sorption and Decantation, g	pH of Tracer Solution after Sorption	Eh of Tracer Solution after Sorption
Required	*Required*	*Required*		*Required*		*Required*	

Mass of Counting Vial, g	Mass of Counting Vial + Aliquot of Tracer Solution (after Sorption), g	Mass of Counting Vial + Aliquot of Tracer Solution (after Sorption) + Scintillation Gel, g	Mass of Counted Tracer Solution (after Sorption), g	Total CPM in Counted Tracer Solution (after Sorption)	CPM/g or ppm in Counted Tracer Solution (after Sorption)	Control Sample Identifications	Control Tube + Cap Mass, g
Required	*Required*			*Required*		*Required*	*Required*
Mass after Tracer Solution was added to Control tube, g	Mass after Sorption Ended in Control Tube, g	% Evaporation during Sorption in Control Tube	pH of Tracer Solution (after Sorption) in Control Tube	Eh of Tracer Solution (after Sorption) in Control Tube	Mass of Counting Vial, g	Mass of Counting Vial + Aliquot of Tracer Solution from Control Tube, g	Mass of Counting Vial + Aliquot of Tracer Solution from Control Tube + Scintillation Gel, g
Required	*Required*		*Required*		*Required*	*Required*	
Mass of Counted Tracer Solution from Control Tube, g	Total CPM in Control Tracer Solution Counted	CPM/g or ppm in Control Tracer Solution Counted	Tracer Solution (Used for Sorption) Sample Identifications	Mass of Counting Vial, g	Mass of Counting Vial + Aliquot of Tracer Solution (Used for Sorption), g	Mass of Counting Vial + Aliquot of Tracer Solution (Used for Sorption) + Scintillation Gel, g	Mass of Counted Tracer Solution (Used for Sorption), g
	Required		*Required*	*Required*	*Required*		
Total CPM in Counted Tracer Solution (Used for Sorption)	CPM/g or ppm in Counted Tracer Solution (Used for Sorption)	Water ID	Type of Scintillation Cocktail Used	ID of Tracer Solution Used for Sorption Experiment			
Required		*Required*		*Required*			